UDC 666.293.52:66.018

LOW-MELTING CHEMICALLY RESISTANT ENAMEL FOR STEEL KITCHENWARE

S. P. Rodtsevich,[1] S. Yu. Eliseev,[1] and V. V. Tavgen'[1]

Translated from Steklo i Keramika, No. 1, pp. 25 – 27, January, 2003.

Technological conditions for obtaining titanium-borosilicate glasses and properties of enamel coating, spreadability of enamels, and luster of coatings are investigated. The effect of boron and alkali metal oxide on the physicochemical properties of titanium-borosilicate enamels is studied. A chemically resistant enamel for steel kitchenware is developed, with improved properties compared to currently used industrial enamels.

Vitreous enamel coatings have a number of valuable properties and are widely used for protecting against corrosion and for improving decorative properties of steel tableware. At present rigid requirements are imposed on glass enamel coatings with respect to migration of coating components into alimentary acid solutions. The known enamels do not meet the increased requirements; furthermore, they contain substantial quantities of scarce boron-bearing materials.

Initial glasses for enamels are multicomponent glasses. However, in selecting components for cover-coat enamels for kitchenware there are substantial restrictions on using numerous elements, which have a favorable effect on technological properties but are inadmissible with respect to toxicology. This clearly complicates the given problem.

Despite more than a century of developing cover-coat enamels for household articles, this problem remains topical. Dozens of vitreous enamel compositions were developed in the USSR (for instance, GOST 24405–80 contains description of 14 vitreous enamel compositions). Researchers in different countries keep developing new enamels with improved properties. The development of low-melting low-boron enamels is especially topical. Foreign manufacturers [1] often introduce BaO, ZnO, PbO and other toxic compounds in compositions of low-melting enamels. The sanitary regulations in the USSR and now also in Belarus forbid using such substances in cover-coat enamels. Domestic low-melting enamels contain substantial quantities of alkali and alkali-earth oxides, as well as Al_2O_3, TiO_2, etc. (RF patent No. 94029961, USSR Inventor's Certif. No. 1615160).

All specified enamels have firing temperature from 720 to 870°C and sufficiently good luster and spreadability. However, one of the main drawbacks of such enamels is the presence of great quantities of boron compounds and, consequently, their low chemical resistance.

[1] Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, Minsk, Belarus.

The enamel ÉSP-140 (GOST 24405–80) currently used for enameling kitchen tableware has good physicochemical properties, but its firing temperature is 840 – 860°C. Furthermore, it is quite sensitive to small variations in technological parameters of frit melting and batch material compositions, which may decrease the chemical resistance of enamel and affect its decorative properties. The use of lower-melting and corrosion resistant enamels can have a substantial cost-saving effect.

A patent research, as well as previous studies performed at the Institute of General and Inorganic Chemistry (USSR Inventor's Certif. Nos. 992447 and 1154228), indicated that a borosilicate system with additives of alkali, alkali-earth, titanium, and zirconium oxides is promising.

The purpose of the present study was to develop a composition of low-boron beige cover enamel for steel kitchenware. This enamel should satisfy all requirements of GOST 24405–80 and Belarus sanitary regulations SanPiN 13-3 RB 01 with respect to their technological properties, and migration of boron and fluorine ions into a boiling 4% solution of acetic acid should not exceed 0.5 mg/liter.

Glasses for enamels were melted in an electric laboratory furnace with silite heaters in quartz crucibles of 1 liter capacity at 1300 – 1320°C for 25 – 30 min with subsequent granulation in water. Preparation of slip, deposition of enamel on samples, and firing of coatings were carried out according to the technology generally accepted in enameling of metals [2].

The crystallization capacity, the TCLE, and the initial softening temperature were determined using the generally accepted methods [3], the capacity of glass to form coating was analyzed by the gradient method, chemical resistance (water and acid resistance) by the granular method according to GOST 10134.0–82 – GOST 10134.2–82, corrosion resistance of coatings determined by GOST 24788–81, and spreadability by GOST 24405–80.

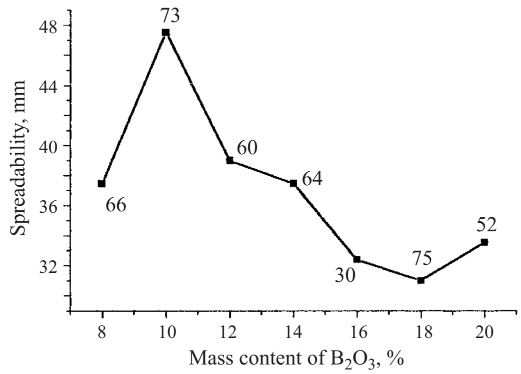

Fig. 1. Effect of B_2O_3 on spreadability of enamel. Digits on the plot indicates coating luster (%).

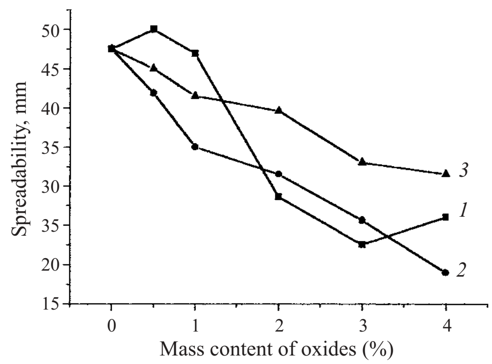

Fig. 2. Effect of MgO (*1*), CaO (*2*), and ZrO_2 (*3*) on spreadability of enamel.

Boron compounds are intense fluxes lowering glass-melting and enamel-firing temperature. We analyzed the effect of boron oxide on chemical resistance of glass and on coating properties. An increased amount of boron oxide in glass (at the expense of SiO_2 and/or TiO_2, R_2O) decreases the chemical resistance of glass and corrosion resistance of coating and, accordingly, results in increased leachability of boron from enameled coatings. Increase in the amount of boron oxide in glass does not have a unique effect of the technological properties of coating. Thus, an increase in the B_2O_3 content from 8 to 10 wt.% enhances spreadability by 10 units, whereas a further increase in the B_2O_3 content up to 18% consistently lowers spreadability by 16.5 mm, then increase from 18 to 20% again increases spreadability by 2.5 mm.

Such parameter as luster behaves ambiguously as well. Initially it grows, then consistently decreases, and then again increases (Fig. 1). This may be due to the fact that under an excessive content of boron oxide, the melt viscosity decreases and creates conditions for growth of rutile crystals exceeding the optimum size (x-ray phase analysis of glass heat-treated at 730°C identified the presence of a crystalline phase represented by rutile and a small quantity by anatase).

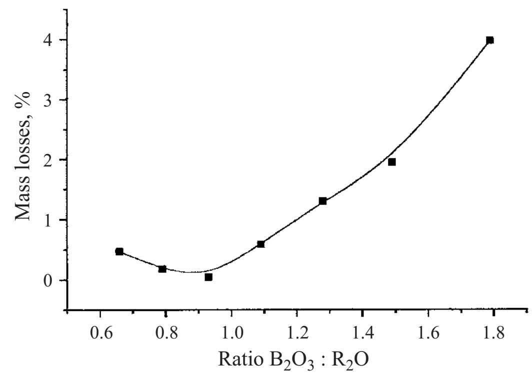

Fig. 3. Effect of ratio $B_2O_3 : R_2O$ on chemical resistance of enamel in 4% solution of CH_3COOH.

An attempt to improve the service properties of coatings using complex glass compositions was not justified. Introduction of CaO and MgO at the expense of TiO_2 and/or B_2O_3 raises enamel firing temperature and lowers its chemical resistance, spreadability of enamel, and luster of coating (Fig. 2). Introduction of a certain quantity of zirconium at the expense of titanium oxide does not produce promising results either, as the chemical resistance of the glass decreases. Therefore, we rejected the idea of introducing magnesium, calcium, and zirconium into the enamel composition.

Alkaline metal oxides substantially decrease firing temperature and raise the TCLE of enamel but, similarly to boron oxide, decrease the chemical resistance of enamel. We investigated the effect of joint introduction of alkali oxides and boron oxide. If they are introduced instead of each other, no positive effect is achieved. However, if they are introduced jointly (for instance, at the expense of SiO_2) in a specific ratio, then even substantial quantities of both components do not have an adverse effect on the chemical resistance of coatings.

It is known [4] that under a certain ratio of alkali ions to boron oxide, the boron ion may change from three coordination to four coordination and, accordingly, can create a more rigid structural lattice in glass. Indeed the experiments showed (Fig. 3) that glasses with the ratio $B_2O_3 : R_2O$ (where R_2O is used for Li_2O, Na_2O, K_2O) close to 1 have the highest resistance in acetic acid solution.

Alkali oxides should be introduced not as a single oxide but as a combination of oxides (polyalkaline effect). For instance, Na_2O is replaced by K_2O, Li_2O, or $K_2O – Li_2O$. This can increase the chemical resistance of enamel (the presence of lithium oxides has an especially favorable effect on chemical resistance of enamel). Investigation of titanium-boron-silicate enamel established that enamels with the alkali oxide ratio $Na_2O : K_2O : Li_2O$ equal to 3 : 2 : 1 exhibit the highest chemical resistance. Replacement of the ratio $Na_2O : K_2O : Li_2O$ by $Na_2O : K_2O$ or by another ratio, or a decrease in the amount of Li_2O in the ternary ratio, produce a sharp deterioration of luster and chemical resistance of enamel (the sum of alkali oxides being equal).

As a result of the studies performed, a low-boron chemically resistant cover-coat beige enamel for steel kitchenware has been developed, which has a firing temperature of 760 – 800°C, spreadability 47.5 mm, TCLE in the temperature interval of 20 – 400°C equal to 94.2×10^{-7} K^{-1}, an initial softening temperature of 515°C, and chemical resistance in 4% acetic acid equal to 0.05% (grain mass loss). There is no migration of boron or fluorine ions into 4% solution of acetic acid.

The enamel passed industrial testing at the Krasnyi Metallist factory in Borisov.

REFERENCES

1. A. Petzold and G. Peschmann, *Enamel and Enameling* [Russian translation], Metallurgiya, Moscow (1990).
2. *Enameling of Metallic Articles* [in Russian], Mashinostroenie, Leningrad (1972).
3. N. M. Pavlushkin, G. G. Sentyurin, and R. Ya. Khodakovskaya, *A Practical Course in Technology of Glass And Glass Ceramics* [in Russian], Stroiizdat, Moscow (1970).
4. S. P. Zhdanov, “Possibility of the calculation of a content of tetrahedral boron in sodium-borosilicate glasses based on the glass composition,” *Dokl. Akad. Nauk SSSR*, **217**(3), 581 – 584 (1974).